



U.S. Army Corrosion Summit 2009

Potential Use of Cold Sprayed Nanostructured Aluminum for Corrosion and Wear Protection



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- ❑ **introduction**
 - **Perpetual Technologies**
 - **nanostructured materials**
 - **ONR program**
 - **cold spray**
 - **nanostructured bulk Al alloys**
 - **corrosion & nanostructured metals**
- ❑ **objective**
- ❑ **target applications**
- ❑ **cold spray of Al**
- ❑ **non-cryogenic processing of nanostructured metal powder**
- ❑ **future work**
- ❑ **summary**
- ❑ **acknowledgements**

introduction

- Perpetual Technologies
- nanostructured materials
- ONR program
- cold spray
- nanostructured bulk Al alloys
- corrosion & nanostructured metals

“offers consulting services relating to conventional and nanostructured coatings”

ACTIVITIES

- provide technical solutions to production problems
- support and/or coordinate R&D projects
- conceive and carry out in-house R&D
- match clients' unique technology/product with applications

CURRENT R&D

- nanostructured oxide coatings
- nanostructured MCrAlY and YPSZ for TBCs
- cold spray application of nanostructured Al, its alloys, and its composites
- nanostructured WC-base coatings for mining and other severe wear applications

ACCOMPLISHMENTS

- development of first non-military application of thermal sprayed nanostructured coating - over 10 mines using nanostructured TiO₂ coatings
- 3 patents relating to thermal spray nanostructured coatings
- co-development of economical processing of nanostructured metal powders

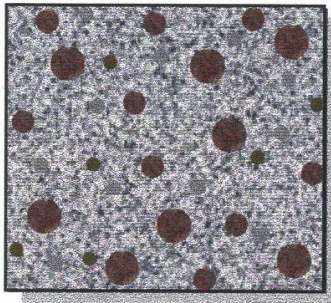
CLIENTS (★) & COLLABORATORS (🔗)

- GE-Global Research Center ★ 🔗
- ExxonMobil ★ 🔗
- Praxair Surface Technologies ★
- ONR ★
- NSWCCD ★ 🔗
- USNA 🔗
- ARL 🔗
- SAIC ★ 🔗
- Syncrude Canada 🔗
- Hydro-Quebec ★ 🔗
- Rice University ★
- McGill University ★ 🔗
- Univ. of California, Irvine & Davis ★ 🔗
- Rutgers University ★ 🔗
- University of Pittsburgh 🔗
- FW Gartner ★ 🔗
- Mogas Industries ★ 🔗
- Scientific Valve and Seal 🔗
- Metal Processing Systems (U.S.) 🔗
- n-WERKZ, Inc. 🔗
- McCarthy Tetrault ★
- Xebec ★

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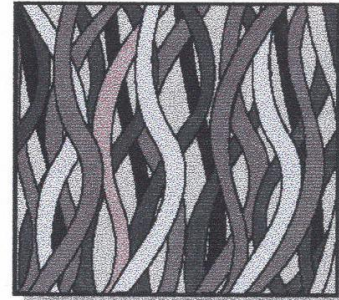
“The term nanostructured is used to describe any material which has some physical feature less than 100 nm in size”



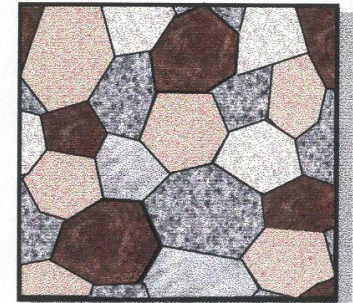
Particle Diameter



Layer Thickness

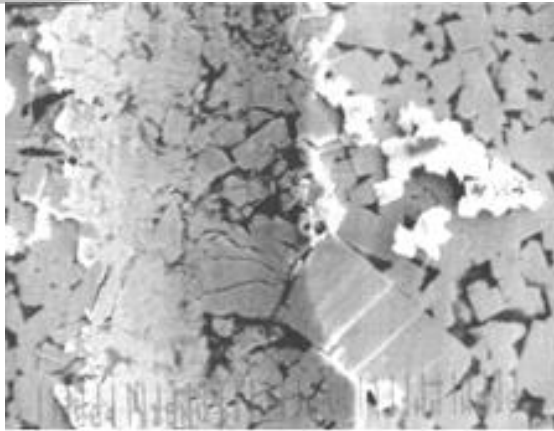


Fiber Diameter



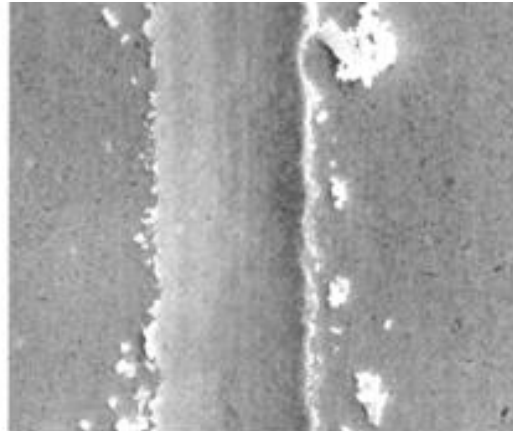
Grain Size

Schematic from ONR



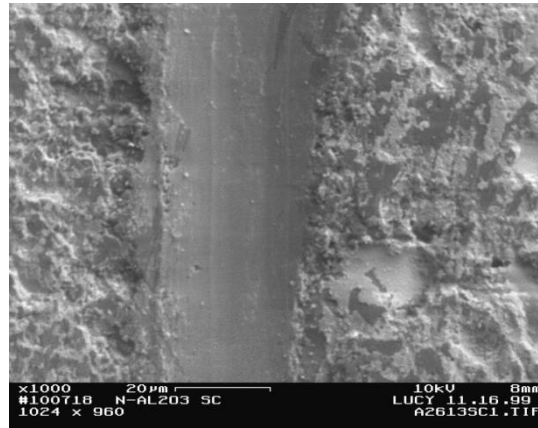
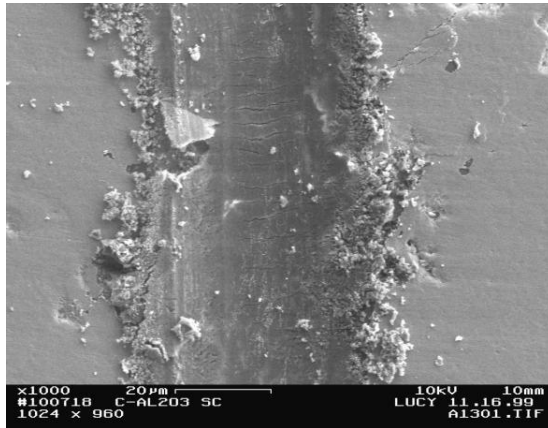
Conventional

(10 micron)



Nanostructured

WC - Co



Al₂O₃- 13TiO₂

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OFFICE OF NAVAL RESEARCH (ONR) FUNDED PROGRAM (FY1996 - FY2001)

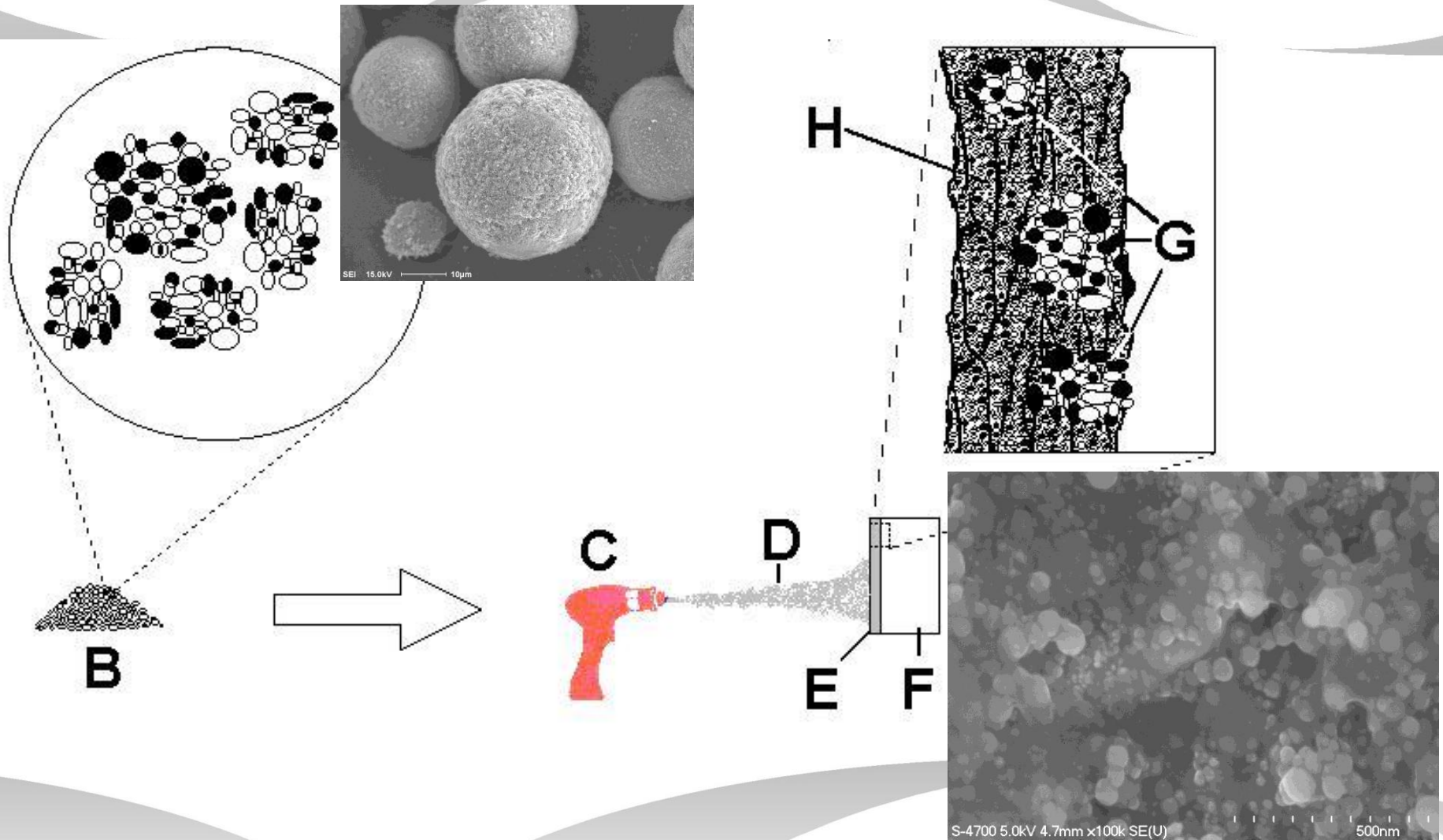
Thermal Spray Processing of Nanostructured Coatings



Lawrence T. Kabacoff
(703)696-0283
kabacol@onr.navy.mil

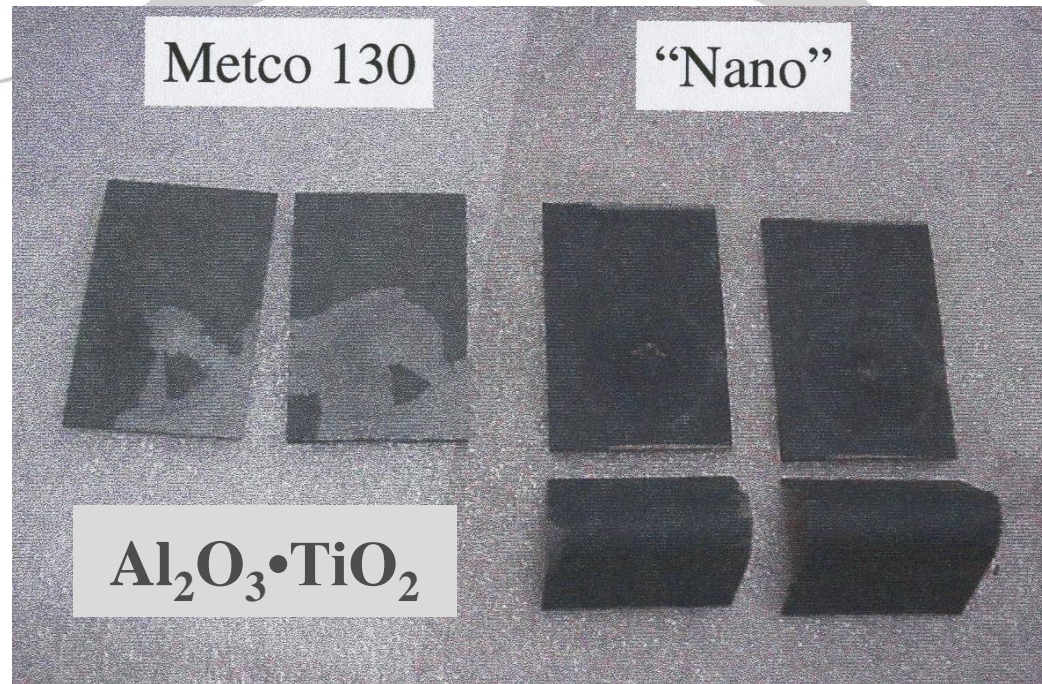
TS n-ceramic coating

developed at UCONN



Nanostructured regions

ONR program - flagship result



from ONR

Advantages of n-coating

- 2x bond strength
- 4x wear resistance
- remarkable toughness
- qualified under MIL STD 1687A
"Thermal Spray Coatings for
Shipboard Machinery"

WHAT WE KNOW...

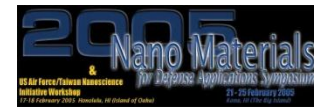
$n\text{-Al}_2\text{O}_3/\text{TiO}_2$ ON PROPULSION SHAFTING – STERN TUBE & STRUT BEARINGS



Courtesy of Ken Scandell - NSWCCD

WHAT WE KNOW...IN-SERVICE T&E

n-Al₂O₃/TiO₂ ON PROPULSION SHAFTING – STERN TUBE & STRUT BEARINGS



Old Method: \$280,000
OEM Weld Repair

ROI COST AVOIDANCE =
\$36,500,000

New Method: \$75,000
Coating Repair

Courtesy of Ken Scandell - NSWCCD

Plasma Thermal Spray n-Alumina
Titanium Ceramic

Surface Grinding & Finishing

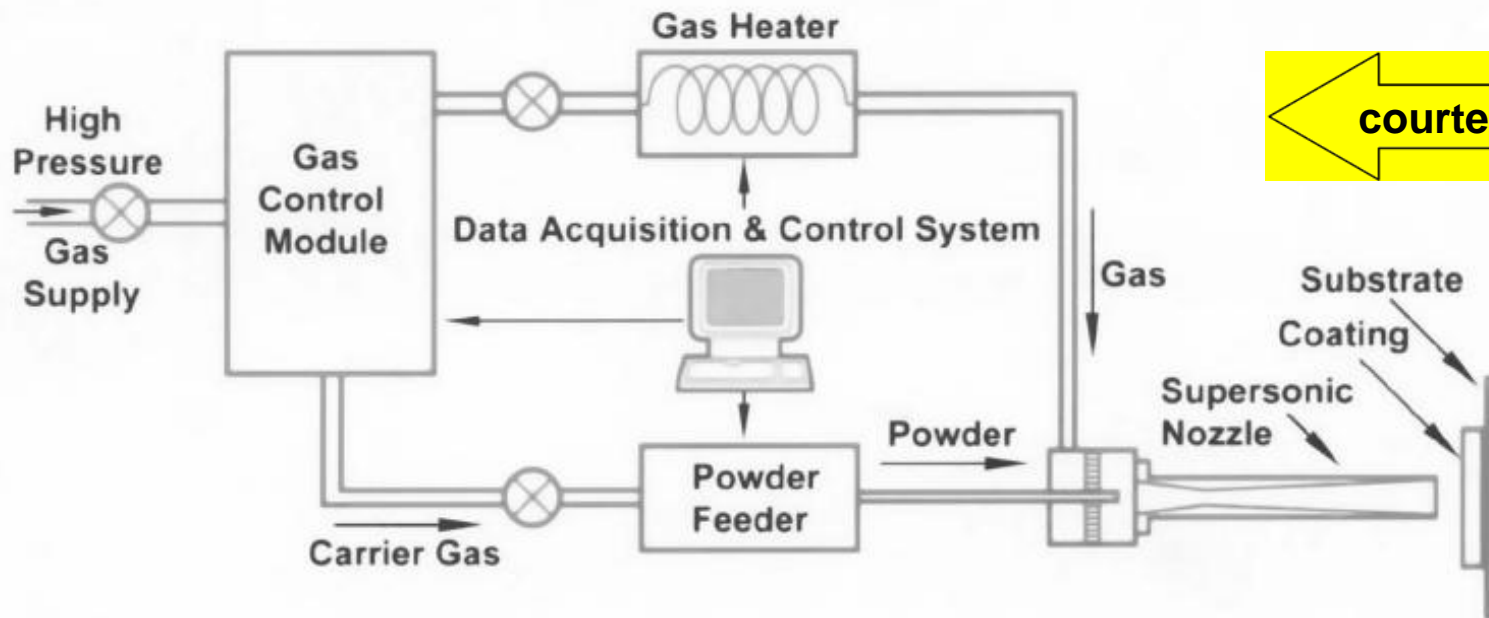
“Nanostructured Coatings Development Team Wins Cheapskate Prize”

- Lawrence T. Kabacoff, A.K. Vasudevan, Robert McCaw and Kenneth Scandell were members of this team
- annual savings are estimated to approach \$100 million

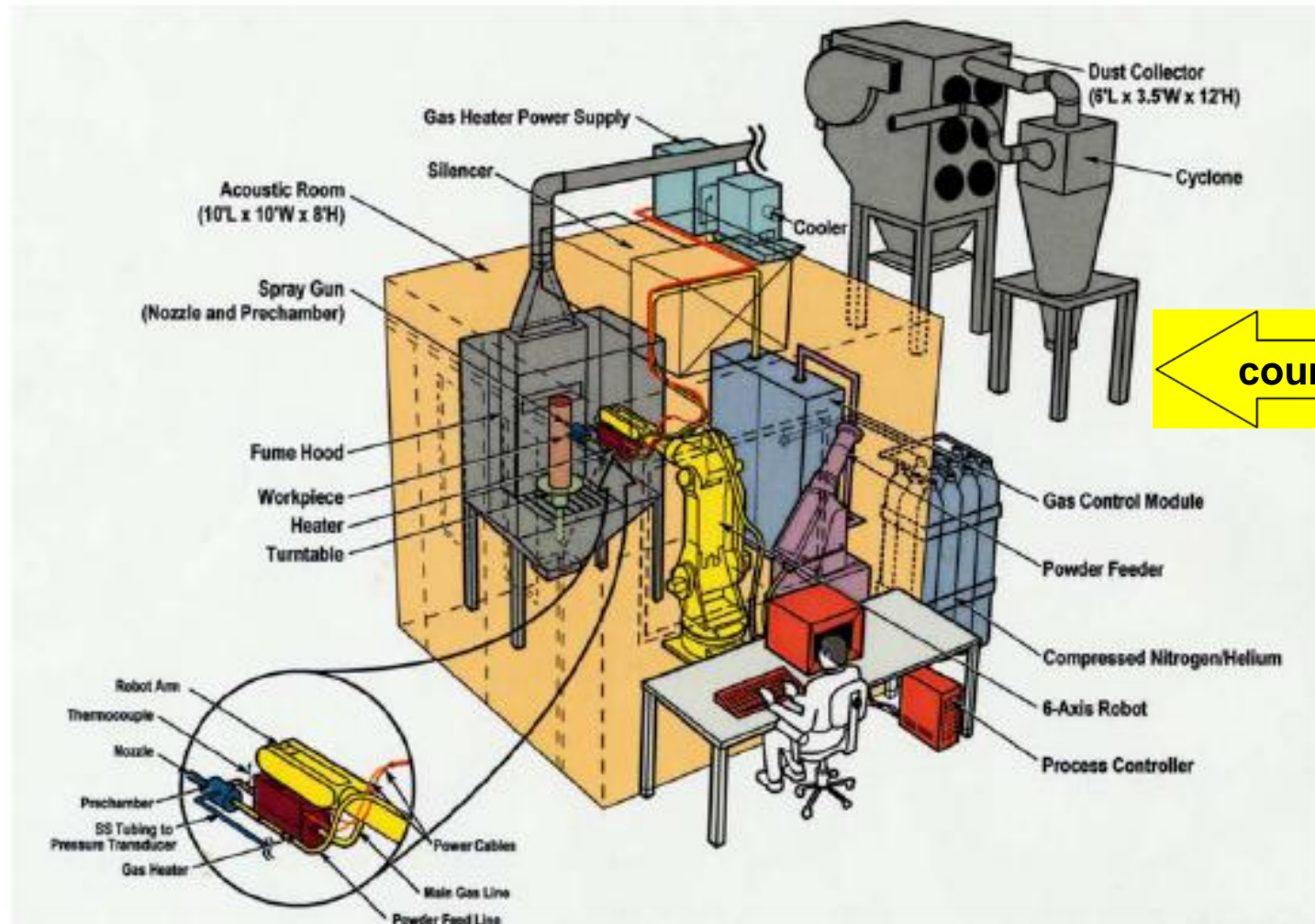
ONR's Cheapskate Award for Affordability celebrates technological improvements that have had the greatest impact on the future availability of affordable technologies for Naval forces.

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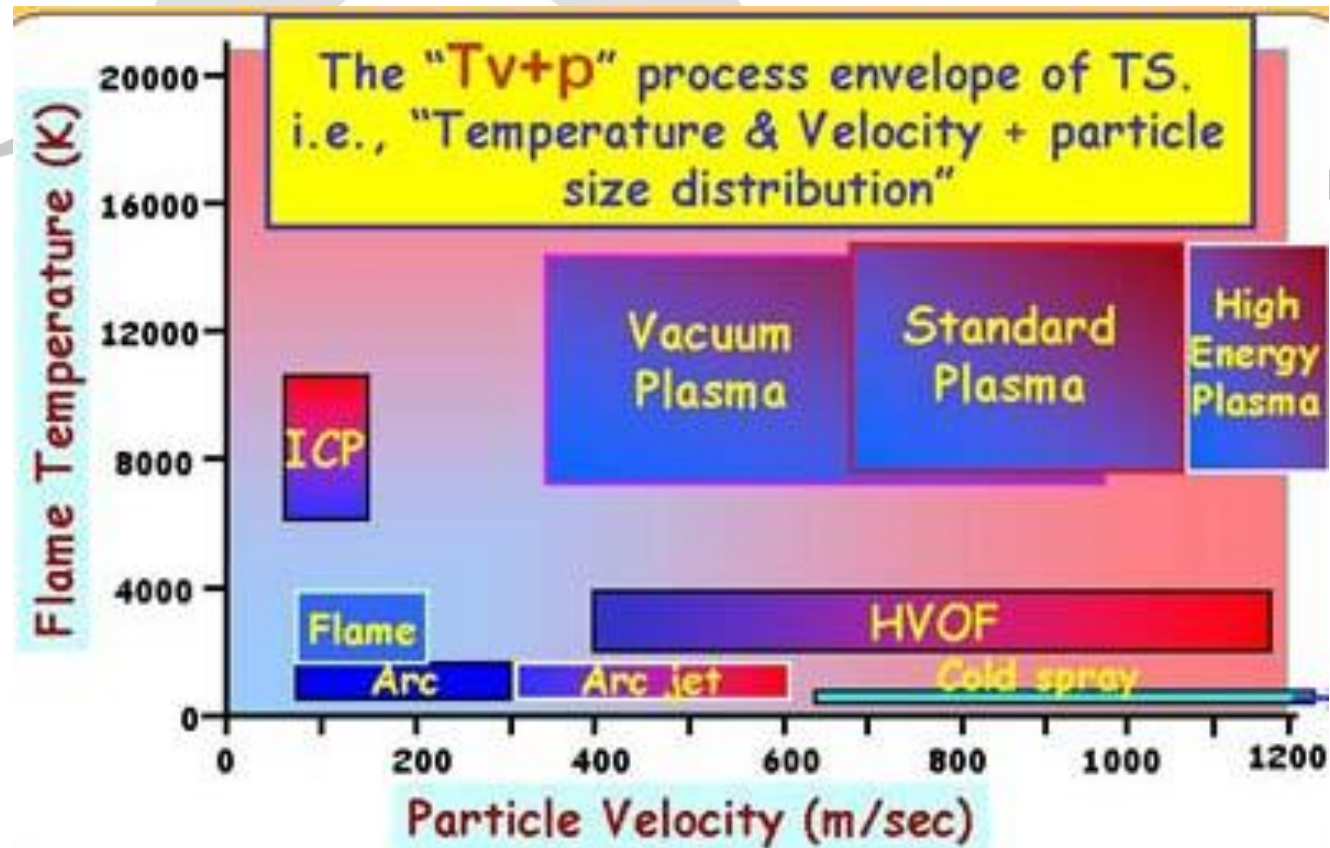


courtesy of ARL



courtesy of ARL

Berndt & Knight



CHARACTERISTICS:

- no phase or compositional change
- **little or no grain growth**
- **low oxide and porosity levels**
- low residual stress (compressive)
- low surface roughness
- high deposition efficiency
- high deposition rate
- recyclable un-deposited powder
- minimal surface preparation

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Rocketdyne Cryomilled Aluminum Processing and Product Forms



Cryomilling Attritor



HIP



Extruded Bar



Extruded Tube



Forging

Rocketdyne Propulsion & Power
UCI Charts, 6-00.ppt, Page 1
6/12/00



Lavernia @ UC,
Davis

- double the strength



MEFFV Approach to Leap-Ahead Technology



Assault Variant

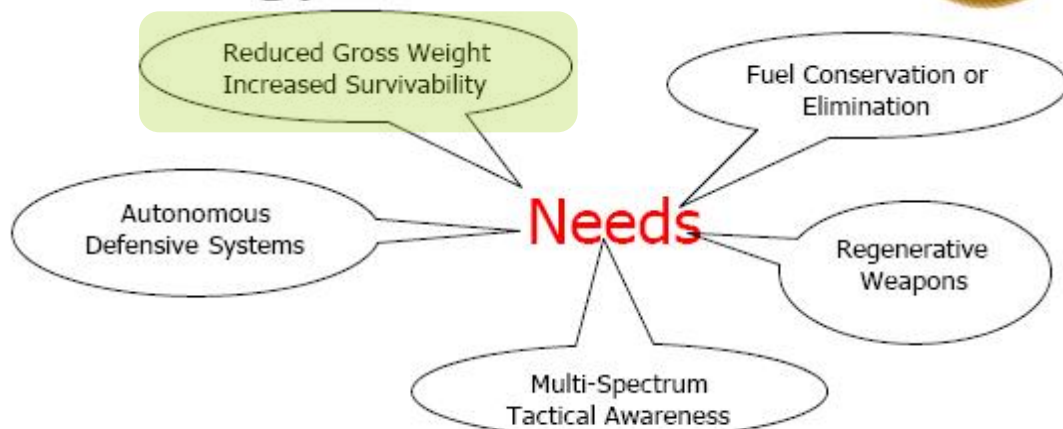


Reconnaissance Variant

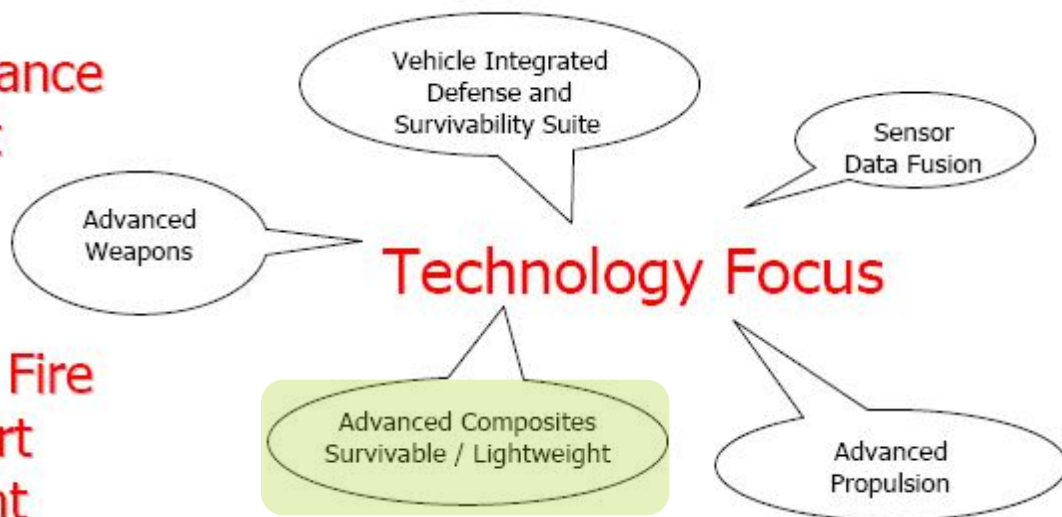


Potential Fire Support Variant

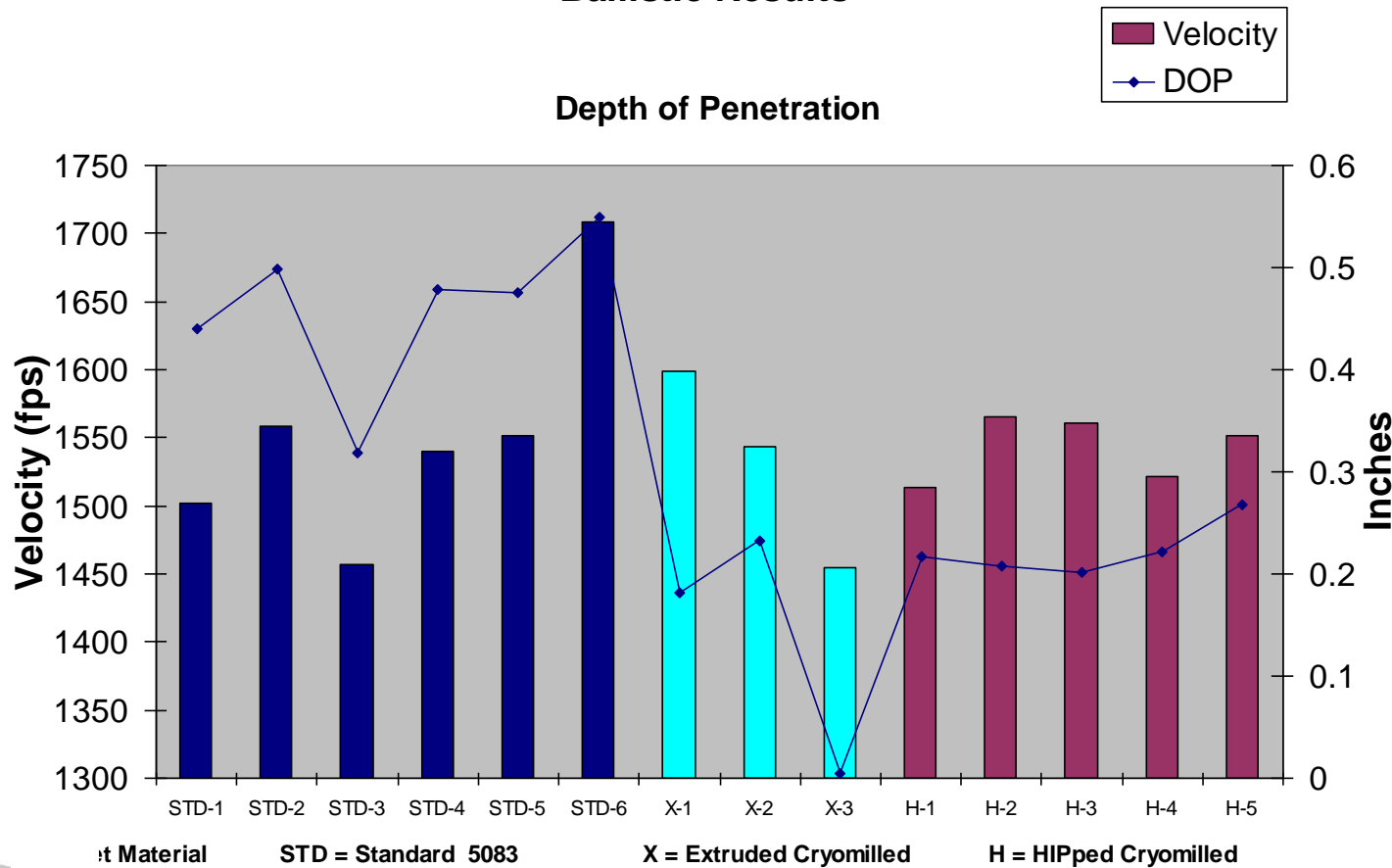
(Post HIMARS/LW155)



high strength/lightweight & armor protective



Ballistic Results



design concepts for cryomilled Al incorporation

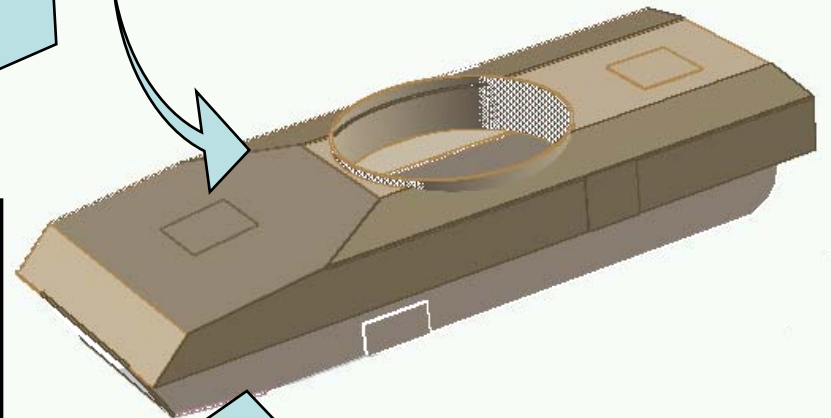


Photo from www.pgbradley.com

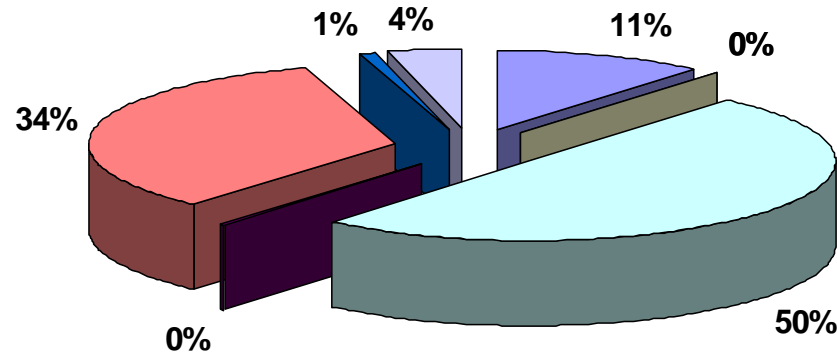
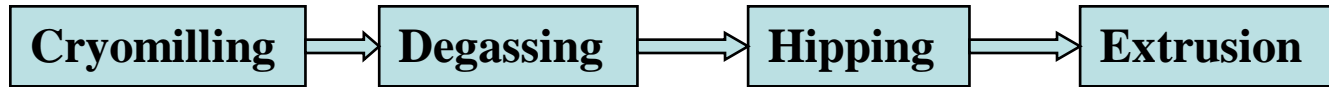
Lavernia @ UC, Davis

Vehicle Upper Hull
"Superior Ballistics Performance and Minimal Weight"
Cryomilled Al w/ Elongation and Bimodal Al

Vehicle Lower Hull
"Highly Loaded, Reinforcing Stiffeners"
Cryomilled Al and Al-MMC Nanocomposite

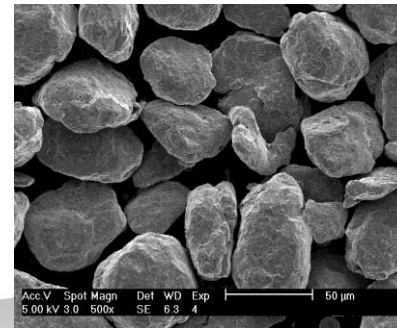
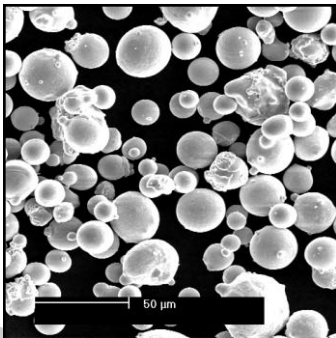


Cost Distribution by Cost Elements



- Primary materials
- Processing Materials
- Additive
- Liquid Nitrogen
- Electricity
- Direct Labor Cost
- Others
- Fixed Cost

Lavernia @ UC, Davis



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“The limited work to date on corrosion resistance of nanocrystalline materials indicates that no generalizations can be made.”

However ...

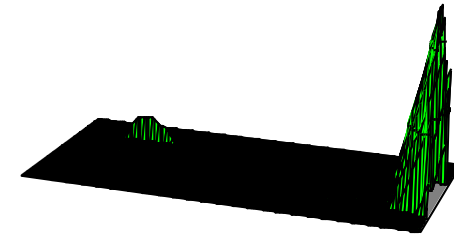
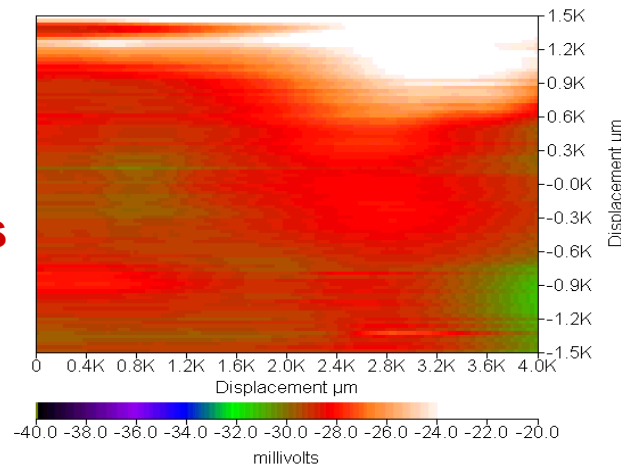
- numerous researchers have reported that nanocrystalline materials show a greater resistance to localized corrosion, i.e., pitting [1-7]

1. Rofagha, R., R. Langer, A.M. El-Sherik, U. Erb, G. Palumbo, and K.T. Aust. 1991. *Scr. Metall. Mater.* 25:2867.
2. Inturi, R.B., and Z. Szklavska-Smialowska. 1992. *Corrosion* 48:398
3. <http://www.parteq.queensu.ca/company/nanometa.html>
4. E. Sikora, X.J. Wei, and B.A. Shaw, *Corrosion*, 2004, vol. 60, no4, pp. 387-398
5. Mala M. Sharma and Constance W. Ziemian, *JMEPEG* (2008) 17:870–878
6. Li Liu, Ying Li, Fuhui Wang, *Electrochimica Acta* 54 (2008) 768–780
7. Li Liu, Ying Li, Fuhui Wang, *Electrochimica Acta* 53 (2008) 2453–2462

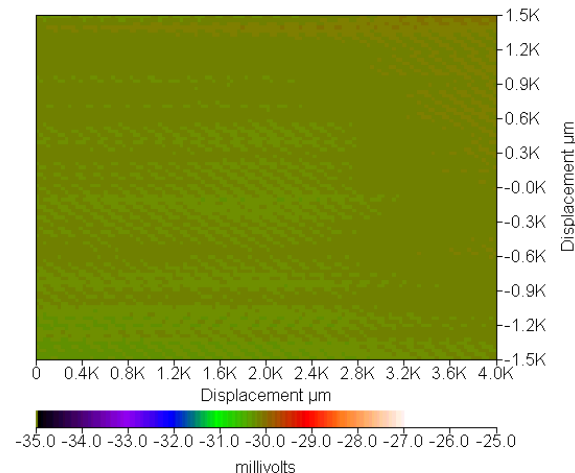
localized corrosion of bulk *n*-Al alloy

SRET Analysis of Bulk *n*-Al Alloys from cryomilled powders

**Sample 1 –
coarser grains
300-500 nm**



**Sample 2 –
finer grains
~ 100 nm**



**pitting is generally the cause of failure or
of replacement for most military
applications; finer grained Al alloy
shows reduced propensity for localized
corrosion**

objective

“To evaluate the possible use of cold spray processing of nanostructured aluminum alloy for corrosion and wear protection”

- use n-Al alloy powder designed for P/M in cold spray application
- must be cost-effective



target applications

LANDING CRAFT AIR CUSHION (LCAC)



- rebuild localized damage
- provide protection



target application – aircraft skins



Objective is to develop an alternative to current ALCLAD process for the protection of aircraft skin from corrosion.

- effective galvanic corrosion protection
- no compromise on fatigue resistance
- easily depot applied
- capable of localized damage repair
- compatible with existing aircraft coatings

cold spray of Al



5056 Al Deposit Using Helium as the Carrier Gas

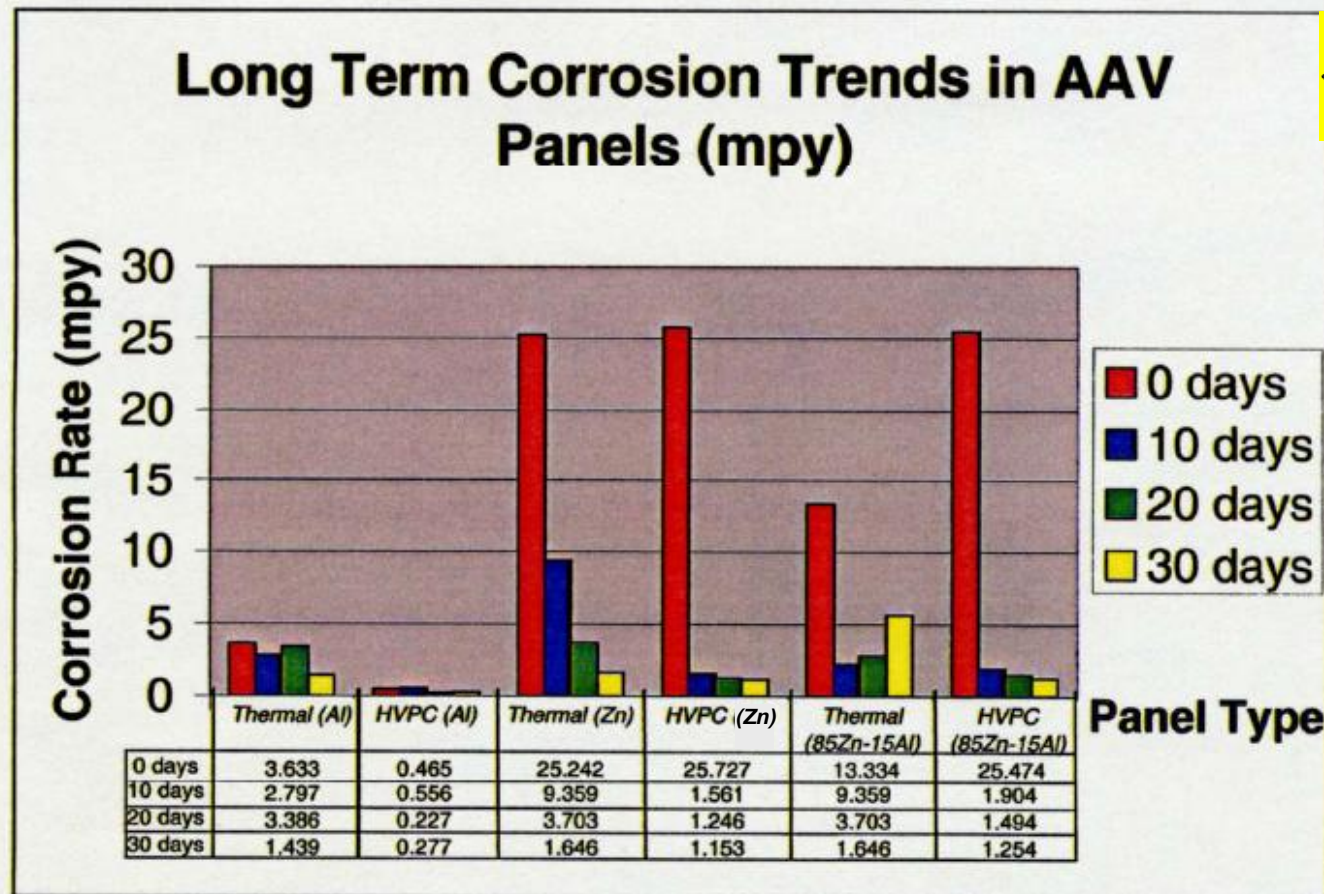
courtesy of ARL

5056 Al
Cold
Spray
Coating

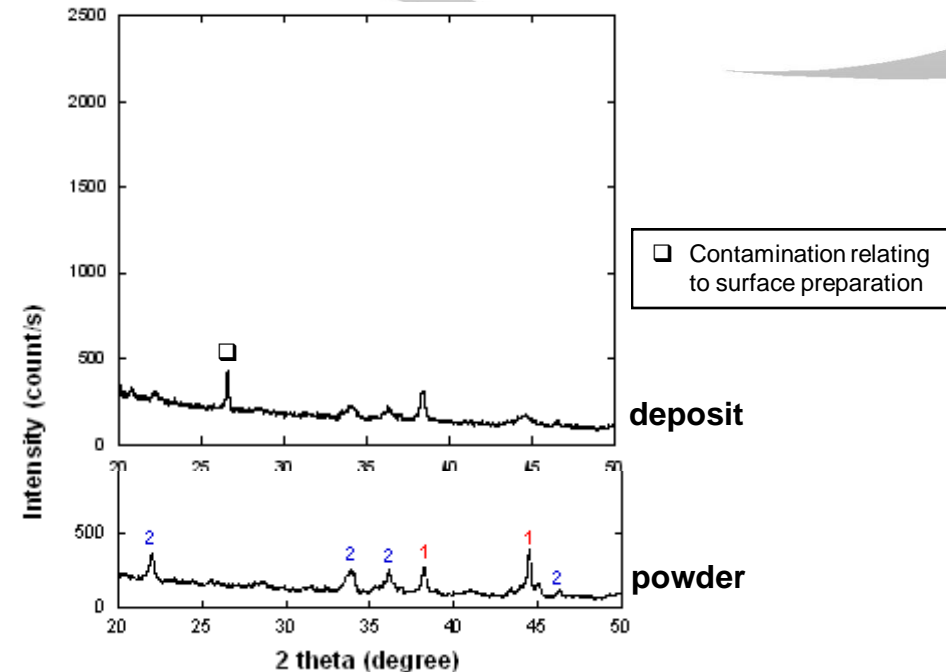
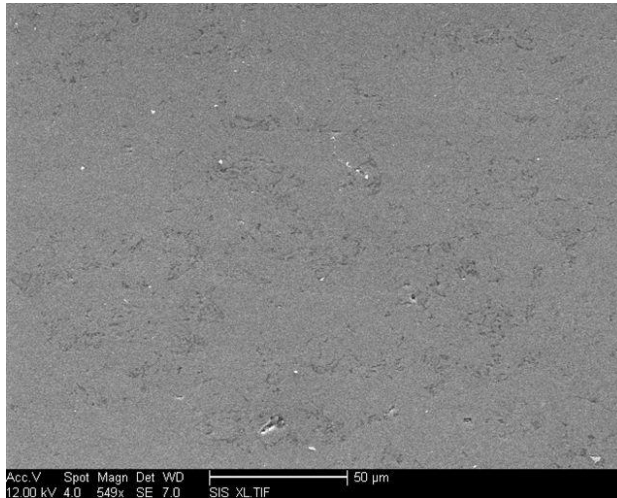
6061-T6
Aluminum
Substrate



Approved for public release



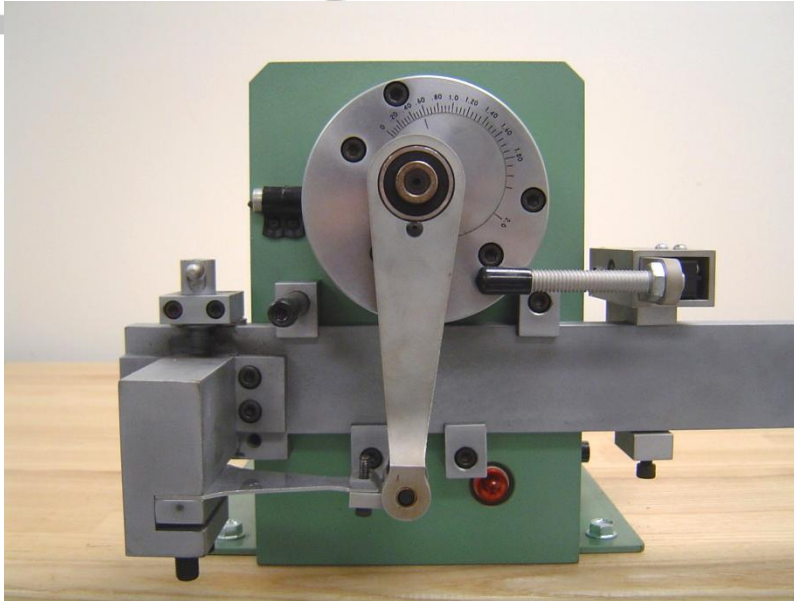
Comparison of corrosion rates of Al, Zn, 85Zn-15Al sacrificial coatings sprayed onto steel.



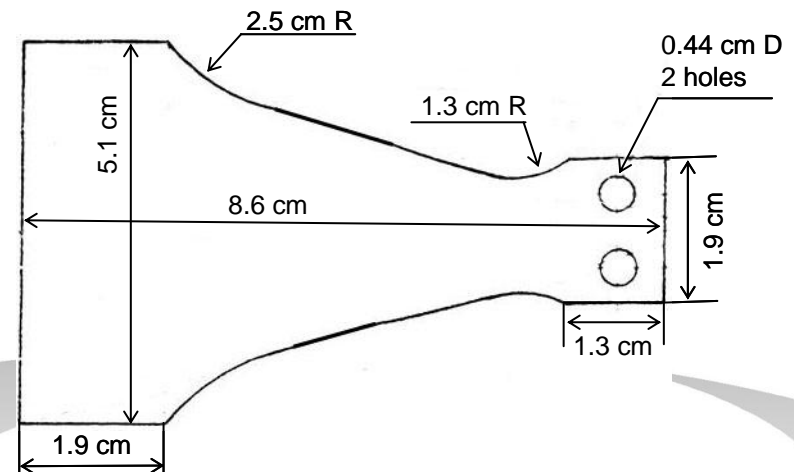
CSP deposits:

- very dense coatings with no sign of oxidation
- little change in composition and grain size

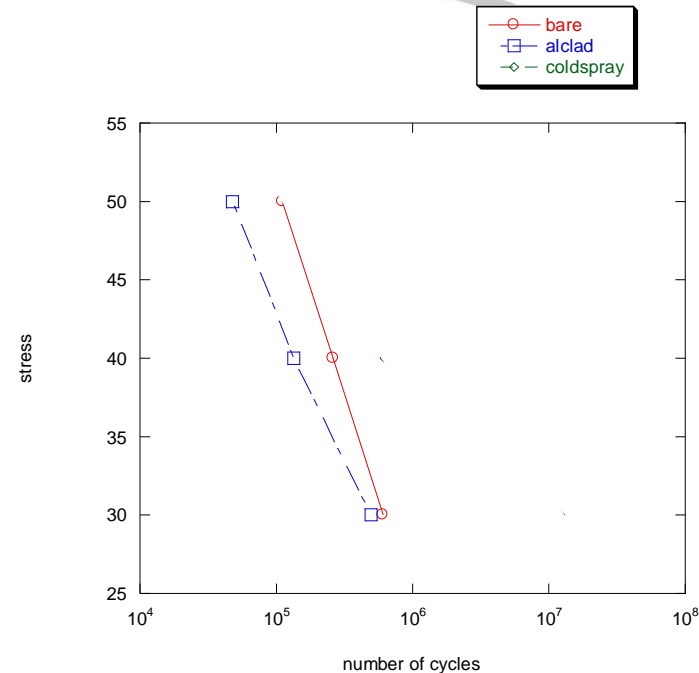
bending fatigue test



- $R = 0$
- $f = 30 \text{ Hz}$
- applied max stress: 30, 40, 50 ksi
- cycles to failure were automatically recorded

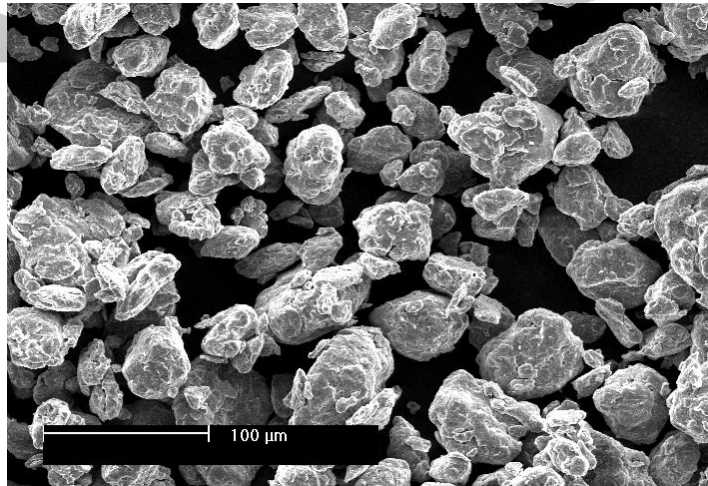


Courtesy of Angela
Moran @ USNA

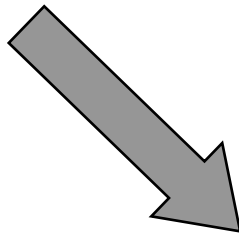
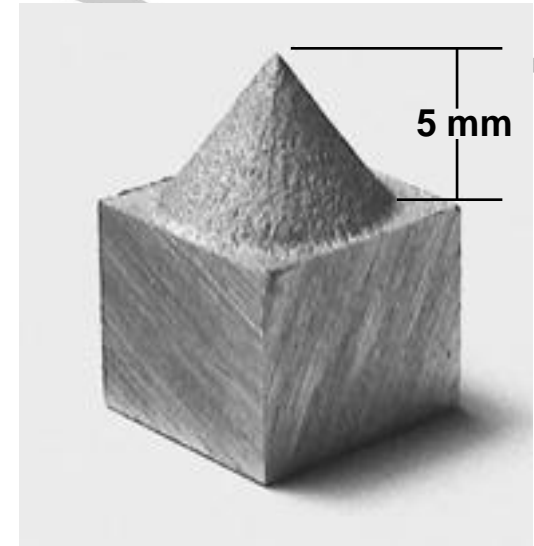


Fatigue test result:

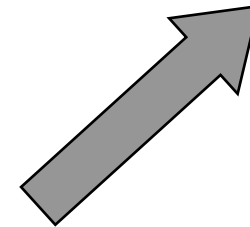
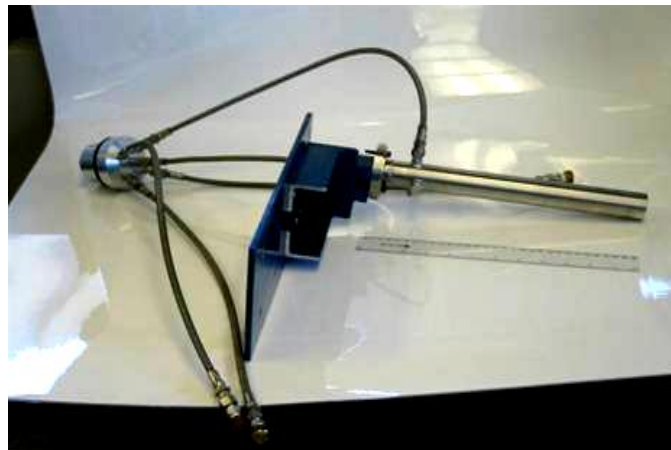
- all CSP samples failed outside the coated region
- CSP applied Al-Co-Ce samples shows excellent resistance to fatigue, even superior to bare metal



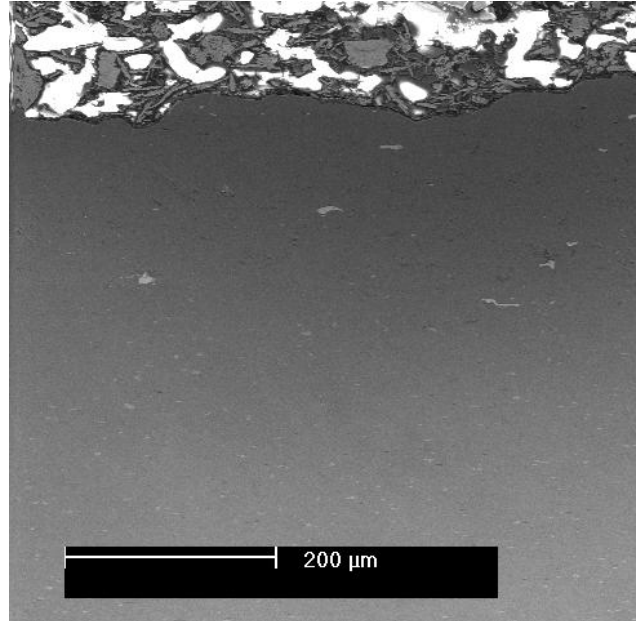
Cryomilled 5083 Al powder



Bertrand Jodoin @
U of Ottawa

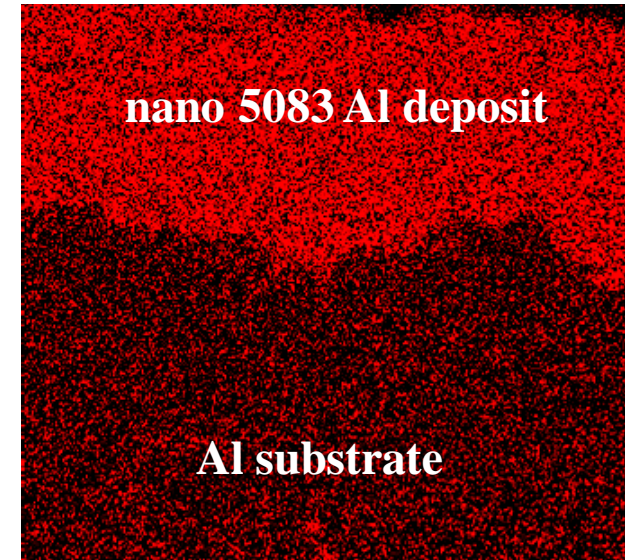


nano 5083 Al



Leo Ajdelsztajn @
UC, Davis

Mg elemental mapping



Sample	Microhardness (HV _{0.3})
cast 5083 Al	87 - 104
CSP 5083 Al	127
CSP n-5083 Al	261



non-cryogenic processing of nanostructured metal powder

- need to reduce cost of powder to pursue military applications



n-metal powder processing

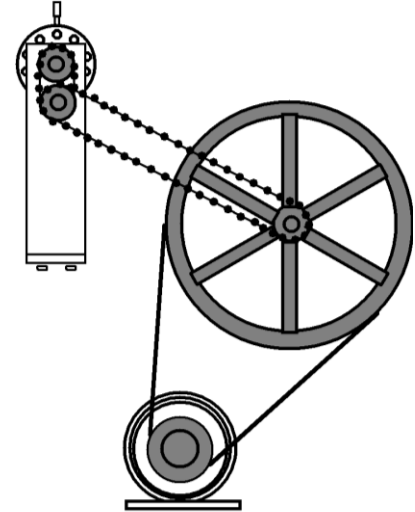
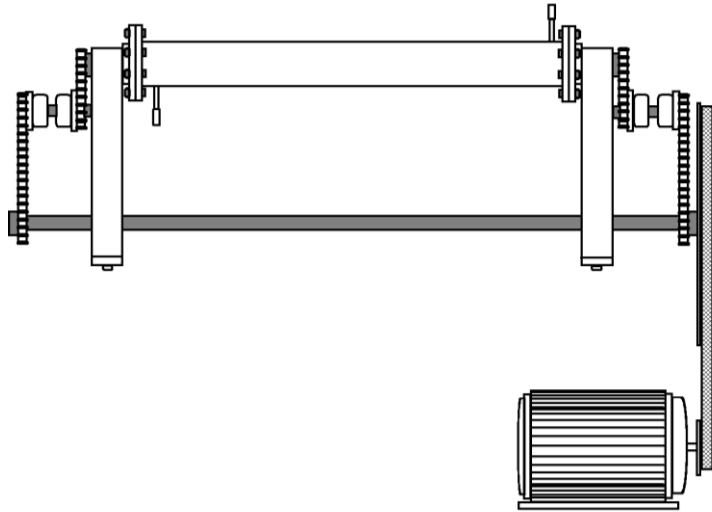
“Objective is to develop an economical means of producing equi-axed nanostructured metal powder using a NON-CRYOGENIC technology”

Immediate Target Materials:

- **AA5083**
- **NiCrAlY**

*Partially Supported by United States Office
of Naval Research*

Dr. Lawrence T. Kabacoff – Program Officer

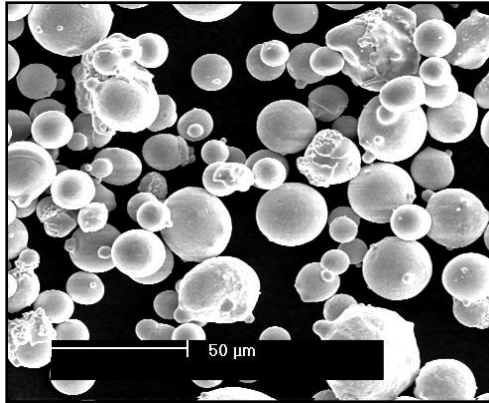


Characteristics:

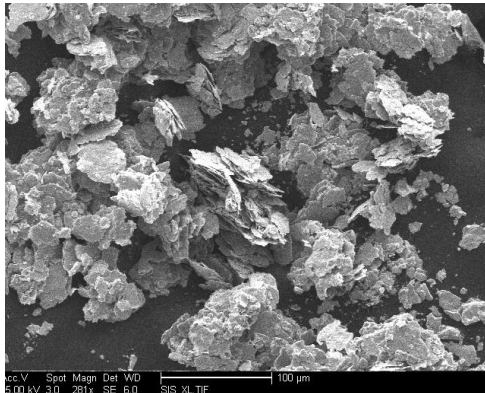
- continuous feed capability
- high energy
- low wall contamination due to little movement of media w.r.t. chamber wall
- very rapid size reduction and dispersion
- good efficiency
- grinds metals, ceramics, intermetallics, and polymers to submicron or nano particle size range.

non-cryogenic milling: lower cost processing of n-metallic powder

as-received

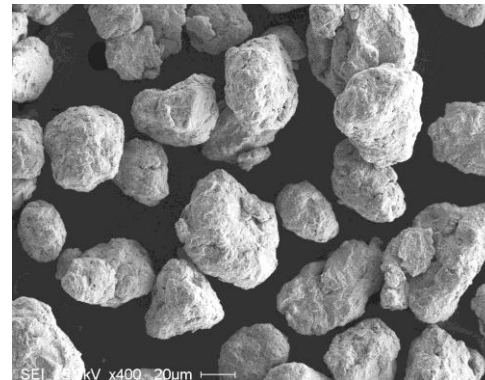
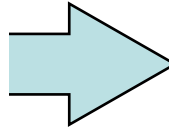


3.5 years



flake particles

2007



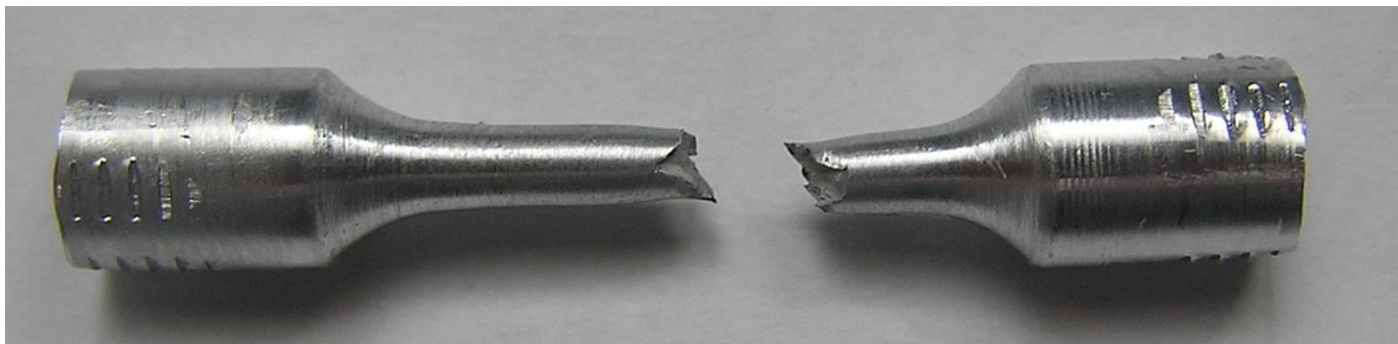
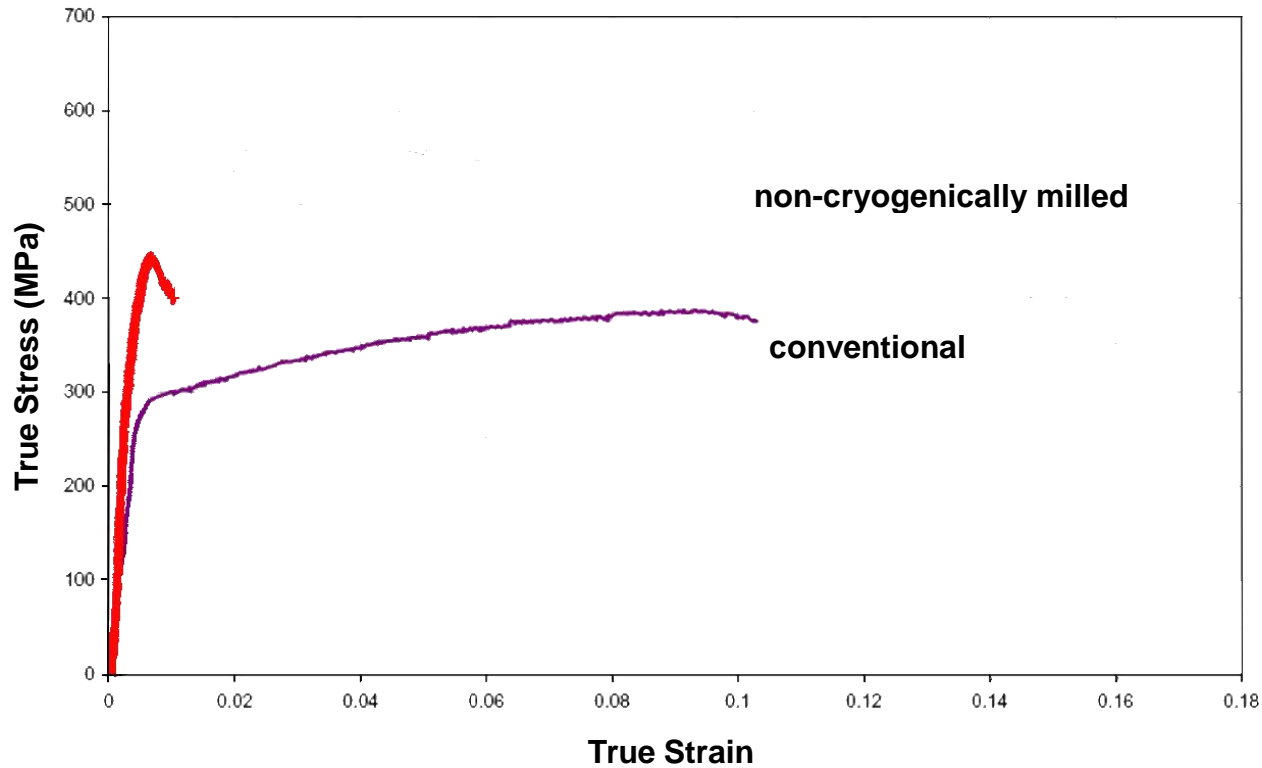
equi-axed powder

“milling metal powders without LN2 is difficult!”

LN2 mitigates:

- excessive welding of particles
- formation of flat particles
- oxidation of particles

non-cryogenic milling: AA5083 bulk sample tensile test results





non-cryogenic milling: AA5083 bulk sample tensile test results

Advantages:

- no liquid nitrogen involved in process
- shorter processing duration
- enhanced strength with high ductility in P/M bulk samples; funded by ONR to optimize milling process and to identify mechanism for high ductility

future work

- ARL will develop cold spray parameters for the **non-cryogenically** milled AA5083 powder
- evaluation of the deposits will be carried out, i.e., metallography, XRD, microhardness
- US Naval Academy will evaluate cold sprayed nanostructured deposits for corrosion resistance and fatigue performance
- wear testing will also be carried out

summary

- **bulk nanostructured Al alloys show a higher resistance to localized corrosion**
- **cold spray process was successfully used to deposit quality nanostructured Al alloy coatings**
- **cold sprayed Al-Co-Ce onto Al alloy samples showed superior fatigue resistance over ALCLADed and substrate-only samples**
- **cold sprayed n-Al alloys have potential for the repair of localized damage of aluminum structures and/or for the protection of metal surfaces against corrosion and wear**

ACKNOWLEDGEMENTS:

- Lawrence T. Kabacoff (ONR)
- A.K. Vasudevan (ONR)
- Enrique J. Lavernia (UC, Davis)
- Leonardo Ajdelsztajn (GE-GRC)
- Mathieu Brochu (McGill U.)
- Bertrand Jodoin (UOttawa)



Thank You!